CURING BEHAVIORS AND MECHANICAL PROPERTIES OF THERMOSETTING VINYL ESTER/ GO NANOCOMPOSITE

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1 Introduction

Vinyl ester resins (VE) have been widely used for construction parts of corrosion resistance, coatings, and electrical devices. VE has excellent chemical resistance, mechanical and thermal properties [1~5]. But VE have shrinkage during the curing behavior. Variety fillers are used for the improvement of shrinkage and satisfy of variety purposes [6]. Carbon nano particles such as carbon nano tube, buckyball and graphene possess unique properties such as high electrical and thermal conductivities as well as mechanical strength. These unique properties attracted many researchers and promise for potential applications for sensor, nanocomposites, batteries and nanoelectronics. In other to investigate electrical and thermal conductivities, many researchers employed carbon nano particles as fillers. Especially, graphene nano sheet which is two-dimensional structure was studied by many researchers for electrical applications. Previous researchers developed methods for preparation of graphene from graphitic structures [7~10]. Graphene has been synthesized by various methods including scotch tape method, electrostatic deposition of graphene, thermal or chemical decomposition of graphitic materials and exfoliation etc. Because of safety and high yield, Hummer's method which is a chemical decomposition of graphitic materials was adapted by many researchers [11]. Graphene oxide (GO) obtained by Hummer's method have various oxygen functional groups. These functional groups hindered electronic conductivity. In order to enhance conductivity of GO, oxidized graphene requires reduction. In case of graphene oxide, electrical conductivity increase with increasing the degree of reduction. Thermal or microwave reduction is used commonly for the reduction of graphene oxide. In this study, graphene oxide was used as filler for the VE resin/ GO nanocomposites. Curing behaviors and mechanical properties of VE resin/ GO nanocomposites were studied employing a differential scannig calorimeter and a dynamic mechanical analyzer. Moduli of the VE/ GO nanocomposites increased with increasing the concentration of GO. The reinforcement by GO in the nanocomposites became less effective after the reduction of GO by microwave irradiation.

2 Experimental

2.1 Preparation of GO

We followed Hummer's method for the preparation of GO. 10g of graphite powder, 250ml H_2SO_4 were mixed in 1000 ml reactor for 15min, subsequently; 35g of $KMnO_4$ was added slowly in an ice bath. The mixture was allowed to react at 35℃ ± 5 for 5hrs and a dark paste was obtained. Then excess water added slowly in an ice bath for dilution. In this step, the mixture was allowed to react under the 50℃. The reaction was terminated by addition of excess of aqueous solution of H_2O_2 (30 wt.%), resulting in a dark brown mixture. Then the mixture was centrifuged and washed several times with water until the system became acid free. The filtered mixture was dried 1day in room temperature, and then dried for 2 days in a vacuum oven at 60℃. For the exfoliation, obtained graphite oxide was exposed to microwave irradiation for 2min employing a general purpose Microwave Oven from LG Electronic. After exfoliation, GO was exposed microwave irradiation additionally for the reduction. To control the reduction of GO, microwave irradiation time was controlled for 1min, 2min and 3min. Reduced GO designated GO-1, GO-2 and GO-3. Table 1 shows sample codes for the graphite, graphite oxide and various GOs

Table 1. Sample code for the graphite and the various graphene oxides

Sample code	Characteristics
Graphite	Synthetic graphite (~ 20 ㎛), Aldrich chemical
Graphite oxide	Oxidation product of graphite by Hummers method
GO-0	Exfoliated GO by microwave irradiation for 2min
GO-1	GO after additional microwave irradiation of GO-0 for 1 min
GO-2	GO after additional microwave irradiation of GO-0 for 2 min
GO-3	GO after additional microwave irradiation of GO-0 for 3 min

2.2 Preparation of VE/ GO nanocomposite

Reduced GOs were dispersed in styrene monomer (SM). SM/ GO mixtures were sonicated for 6hr. After sonication, SM/ GO mixtures were heated at 40℃. Solid state VE which is experimental grade from Cay Valley Korea was heated at 120℃ for the melting. Prepared SM/ GO mixtures were mixed with melted VE. And then temperature deceased at room temperature. Tert-butyl perbenzoate (TBPB) added 1phr for the resin as initiator. Curing of VE/ GO mixtures was progressed at 120℃ for 1hr. Post cure was progressed at 130 ℃ for 2hr.

3. Results and Discussion

Table 2 shows results of element analyses of graphite, GO, and reduced GO. After oxidation of graphite, oxygen content increased largely in GO due to the introduction of many function groups such as epoxy group, carboxyl group, hydroxyl group on the surface of the GO. After exfoliation, oxygen content in GO-0 was decreased and carbon content was increased due to thermal reduction by microwave irradiation during the exfoliation. Oxygen content of reduced GOs was large decreased by microwave irradiation.

Table 2. Element analysis of graphite, graphtie oxide and reduced graphene oxides

Sample code	Weight fraction (wt%)				
	C	H	N	S	O
Graphite	96.29	0.16	0.97	0.21	1.37
Graphite oxide	46.26	2.61	1.02	3.22	47.49
GO-0	69.69	1.28	0.4	2.79	23.36
GO-1	84.12	1.00	0.49	2.21	10.75
GO-2	86.37	0.76	0.50	2.91	7.68
GO-3	87.76	0.60	0.48	2.24	6.43

Figure 1 shows the FT-IR spectra of graphite and the various graphene oxides. The spectrum of graphite oxide illustrates the presence of carboxyl group (at 1622 cm^{-1}), epoxy group (at 1050 cm^{-1}) and hydroxyl group (at 3400 cm^{-1}). Most of the chemical groups were introduced during the oxidation process. The changes in structure during the reduction process are reflected in the FT-IR spectra of GOs. After exfoliation, epoxy group and hydroxyl group were large decreased in GO-0 by microwave irradiation. Function groups decrease with increasing reduction time.

In other to confirm the change of mechanical properties by GO, dynamic mechanical analyzer (DMA; Q 800, TA instrument) was employed. Figure 2 shows the storage moduli of VE/ GO nanocomposite. Content of GO was controlled to 0.5, 1.0, 1.5 and 2.0phr. Figure 2-(1) shows the mechanical properties of VE/ GO-1 nanocomposite. In this data, storage modulus increase with increasing content of GO. In case of GO-3 shows same result like GO-1. In compare GO-1 and GO-3, VE/ GO-1 nanocomposite shows high modulus in high temperature. Function groups of GO-1 more exist than GO-3. Function groups can interaction

with VE resin such as hydrogen bond. Figure 2-(3) show the loss modulus of VE/ GO-1 nanocomposite. Glass transition temperature (T_g) of nanocomposite is higher than neat VE. These results indicate that the GO carry out the role of reinforced material.

Figure 3 shows surface resistivity of VE/ GO nanocomposite. VE/ GO-3 nanocomposite have lower surface resistivity than GO-1 and GO-2 with same filler volume fraction.

In addition, GO content increased with decreasing surface resistivity. The surface resistivity values are determined below equation as follows:

$$\rho = \rho_0 (V - V_c)^{-t} \quad (1)$$

Where ρ is surface resistivity and ρ_0 is prefactor of surface resistivity value, respectively; V is the volume fraction of nanocomposite, respectively; V_0 is percolation threshold for surface resistivity; respectively, and t is the critical exponent for surface resistivity.

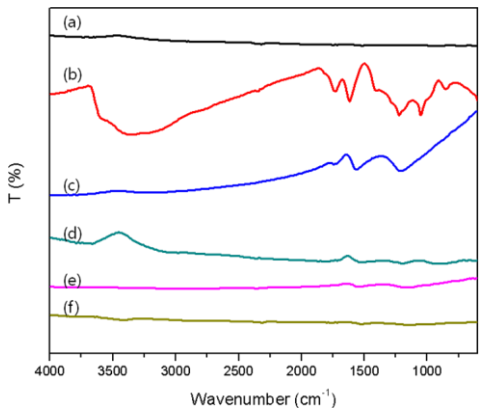

Figure 1. FT-IR spectra of graphite and the various graphene oxides

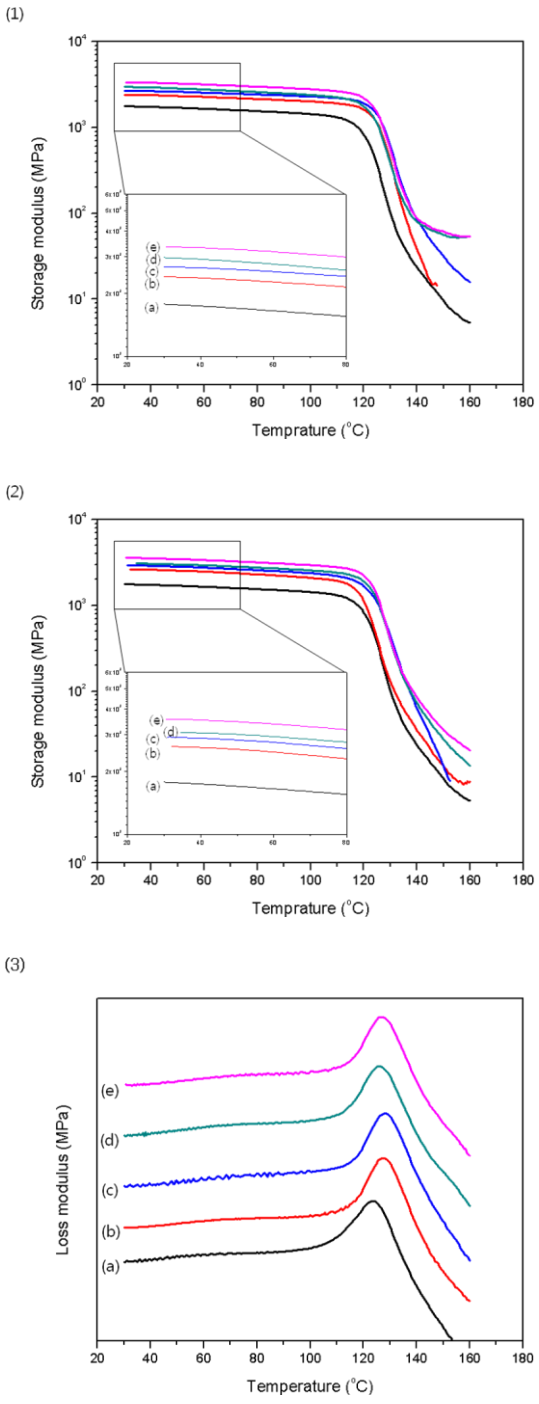

Figure 2. Results of dynamic mechanical analysis of VE/ GO nanocomposites: (a) VE; (b) VE-0.5 (c) VE-1.0; (d) VE-1.5; (e) VE-2.0. (Figure 2-(1) and Figure 1-(3): irradiation time: 1min, Figure 2-(2): irradiation time: 3min)

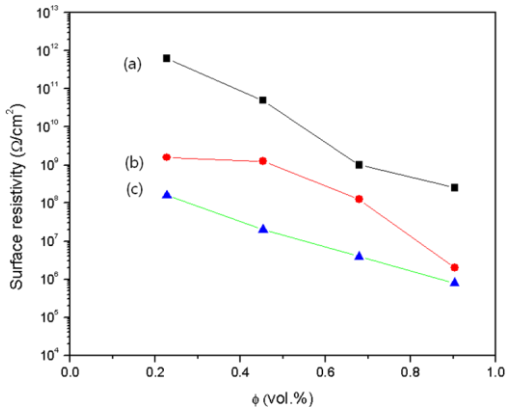

Figure 3. Surface resistivity of VE/ GO nanocomposites versus volume fraction (φ) of GO:

(a) VE-1; (b) VE-2; (c) VE-3.

In case of GO-3, volume fraction of percolation threshold is 0.0079. Compare with GO-2 (V_c: 0.0081) and GO-1 (V_c: 0.0084), GO-3 is lower than other samples. This result implying that GO-3 is a more efficient conductive filler. Because of function groups hinder the electrical and thermal conductivity.

GO affect the curing behavior. Table 3 shows the result of thermal analysis by different scanning calorimeter (DSC; Q-20, TA instrument) thermograms. Neat VE resin begins curing behavior at 123.8℃. Concluded GO samples are delayed curing behavior. Increase of GO content and degree of reduction with increasing onset temperature. GO has contributed increase of viscosity by GO. Due to the high viscosity which hindered diffusion effect in initiator delayed curing behavior.

4. Conclusion

GO affected mechanical properties, electrical conductivities and curing behaviors. DMA data shows improvement of modulus and T_g. this result implying that the GO carry out the role of reinforced material. Function groups are hindered electrical and thermal conductivity. High degree of reduction indicated that function groups are removed. Surface resistivity decreased with increasing the GO content and degree of reduction. This result shows the GO carry out the role of electrical filler. But GO affected curing behavior. Onset temperature was delayed by GO

Table 3. Result of thermal analysis of VE/ GO nanocomposites.

Sample code	Thermal property		
	T_{onset}(℃)	T_{peak}(℃)	ΔH(cal/g)
VE	123.8	140.7	-87.8
VE-1-0.5	128.4	141.3	-84.3
VE-1-1.0	131.8	142.3	-84.0
VE-1-1.5	134.1	144.8	-83.6
VE-1-2.0	134.8	145.4	-83.3
VE-2-0.5	129.6	140.4	-84.2
VE-2-1.0	132.7	144.3	-84.0
VE-2-1.5	135.4	144.5	-83.5
VE-2-2.0	134.7	145.3	-82.2
VE-3-0.5	131.1	141.4	-83.7
VE-3-1.0	135.8	146.1	-83.3
VE-3-1.5	134.5	146.3	-82.4
VE-3-2.0	136.4	147.2	-82.3

content and degree of reduction. Because of high viscosity which increased with increasing the GO content hindered diffusion effect in initiator.

5. References

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